

Ab initio calculation of a Pb single layer on a Si substrate: two-dimensionality and superconductivity

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We report on first principles calculations of superconductivity in a single layer of lead on a silicon substrate including a full treatment of phononic and RPA screened coulomb interactions within the parameter free framework of Density Functional Theory for superconductors. A thorough investigation shows that several approximations that are commonly valid in bulk systems fail in this constrained 2D geometry. The calculated critical temperature turns out to be much higher than the experimental value of 1.86K. We argue that the only plausible explanation for the experimental T_c suppression is the onset of fluctuations of the superconducting order parameter.

Nature shows a clear correlation between superconductivity and dimensionality as all superconductors with a high critical temperature (T_c), cuprates, pnictides and MgB_2 , have sharp two-dimensional properties. Understanding this connection is among the most important targets in contemporary solid state research. It is likely that relevant physical mechanisms work differently in reduced dimensionality and that approximations and theoretical methods developed through the experience accumulated on three-dimensional systems have to be modified for constrained geometries. Moreover fluctuation instabilities of the order parameter may play an important role[1].

The conclusive test to check the theoretical understanding is to perform *ab initio* calculations and compare directly with experiments. Currently, such a test cannot be done for pnictides and cuprates as the pairing mechanism is still under debate. However, it can be done for phononic superconductors.

In this work we present the results of this type of analysis for lead, as this phononic superconductor is correctly described in bulk by *ab-initio* methods[2, 3] and is experimentally realized in the two-dimensional limit by deposition on a silicon 111 substrate[4–7].

This Si-Pb system is constructed as shown in Fig. 1. We model the Si substrate by a 111 oriented slab, which is passivated on the opposite side of the lead surface using hydrogen[8, 9]. A relatively large width of five Si-bilayers is chosen in order to reduce spurious size effects of the substrate on the Pb layer. For the same reason we constrain the hexagonal (xy) Si unit cell to its bulk size. Lead is placed in the so-called striped incommensurate (SIC) configuration. Since we work with periodic boundary conditions, a vacuum of ~ 8 Å separates the periodic replica of the system. Within these constraints a full relaxation is performed. Relaxations, electronic structure, phonons and electron-phonon interactions have been calculated within Kohn-Sham (KS) density functional theory (DFT)[10]. The calculated electron phonon coupling strength results in $\lambda = 0.78$. If we use the McMillan formula[14] with a standard value for the parameter $\mu^* = 0.10$ we obtain an estimation for the critical temper-

ature of 1.98K. This is in very good agreement[15] with the experimental T_c of 1.86K[4]. With this result one has to conclude that superconductivity in this 2D limit can be understood from the electronic coupling alone and no fluctuations are necessary to explain the physics of this system.

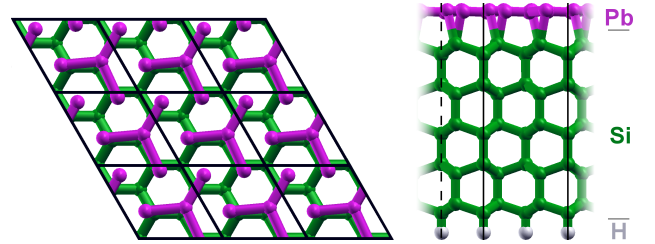


Figure 1. (color online) SIC configuration of Pb on the Si (111) substrate. On the left we present the top view, and on the right the side view. Black lines mark the simulated unit cell.

Is this really the end of the story? Is it correct to assume the validity approximations known to work well in bulk superconductors also for this low dimensional system? The answer is no, and to show this we proceed to deeper investigation.

In order to avoid any adjustable parameter (as the above named μ^*) we use density functional theory for superconductors[2, 16–25] (SCDFT), where electronic and phononic couplings are included on the same footing.

Electronic and phononic properties - A very relevant property in the electronic structure (Fig. 2) is the presence of both Pb and substrate metallic bands. This means that Pb deposition acts as a dopant to the Si substrate which develops a surface metallic region. This metallic region fades away within a few layers. The presence of this additional metallic band is relevant for two reasons. First it may provide a contribution to the electron-phonon coupling and, second, it may stabilize fluctuations of the order parameter of the superconducting phase by effectively enhancing the three-dimensionality of the condensate. These Si metallic bands can be removed by using an n-doped substrate. We explicitly consider this case by substituting one Si

	$\lambda^{Pb,Pb}$	$\lambda^{Pb,Si}$	$\lambda^{Si,Si}$	λ_{av}	$\max[\lambda_i]$	$N_{Pb}(0)$	$N_{Si}(0)$
undoped	0.95	0.13	0.06	0.78	0.98	0.97	0.60
doped	1.03	0.00	0.00	1.03	1.03	1.07	0.00

Table I. Electron phonon coupling coefficients. $\lambda^{i,j}$ is the Fermi Surface sheet resolved coupling matrix. $\lambda_{av} = \frac{1}{N(0)} \sum_{i,j} \lambda^{i,j} N_i(0)$ is the average electron phonon coupling where $N_i(0)$ are the Fermi surface resolved DOS and $N(0)$ is the total DOS. $\max[\lambda_i]$ is the maximum eigenvalue of λ that in BCS acts as the effective pairing to determine the critical temperature[26].

atom (in the deep bulk) with a virtual mixture of P and Si, corresponding to a doping of 1 part per 240 Si. Doping has a small effect on the filling level of the Pb bands, but completely saturates the Si- hole pockets (see Fig. 2). This doped system is experimentally realized [4] and allows for direct comparison with results obtained in this study.

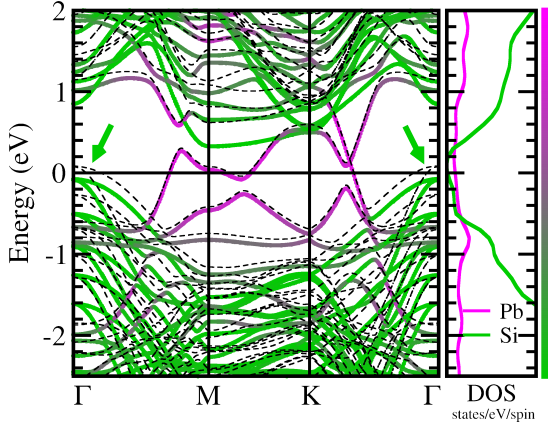


Figure 2. (color online) Band Structure (left) and density of states (right) near the Fermi Energy. Thick lines correspond to a phosphorus doped system (1 part per 224), and the color scale corresponds to the projection on the Pb states. Dashed lines are the bands in the undoped system. The P doping has a negligible effect on Pb bands while it completely fills the silicon hole pockets (indicated by green arrows).

The degree of two-dimensionality of the SC phase, i.e. how the condensate extends into the substrate, is determined by the lead-substrate interaction. We can distinguish three main effects that describe how the Pb surface and the substrate are coupled: chemical hybridization, electron phonon coupling and Coulomb interaction.

The *chemical hybridization* between surface and substrate states can be made visible by projecting the KS states on the Pb atomic orbitals. This analysis shows that the KS states near the Fermi energy are either located in the lead surface or inside the silicon bulk, with no overlap (see Fig. 2).

The *electron-phonon coupling* is computed for the KS system via linear response[10]. Phonons may generate

	T_c	$\Delta^{Pb}(0)$	$\Delta^{Si}(0)$	T_c^*
undoped	3.42	0.71	0.32	2.01
doped	3.54	0.74	—	2.74

Table II. Calculated critical temperatures, T_c (in K), within SCDFE and superconducting gap, Δ (in meV), on the Lead and Si Fermi surfaces. T_c^* is the critical temperature estimated using an average coupling on the Fermi surfaces, ignoring the energy dependence of dos and screened coulomb interactions (corresponding to a μ^* like approximation).

pairing between bulk and surface states. In Tab. I we report the FS-resolved el-ph coupling[27]. By considering the average coupling and ignoring the energy dependence of density of states and screened coulomb interactions (by approximating them with the value at the Fermi energy) we have a formal equivalence of SCDFE with the McMillan method. The resulting critical temperature of lead on the undoped substrate is $T_c = 2.01K$ and T_c rises to 2.74K for the doped Si substrate. The difference in critical temperatures between the doped and undoped system is caused by the fact that the undoped material has an mean coupling which is much weaker than the lead-lead intra-surface coupling alone. This implies that the isotropic approximation is unjustified and leads to an underestimation of T_c . Multiband-superconductivity must be explicitly accounted for as in the well known case of MgB_2 .

Moreover the electrons are subject to a *screened Coulomb* scattering which we treat within the RPA[28, 29]. This kind of interaction in bulk materials is often overlooked, since, acting both as a repulsive (directly) and attractive interaction (via Coulomb renormalization mechanism[30–33]) it appears very often to be largely material independent. This shows up in Eliashberg based methods[14, 34] in the well-known rule of thumb to take $\mu^* \sim 0.1$. A crucial advantage of SCDFE is that via the matrix elements of the RPA-screened Coulomb interaction the Coulomb renormalization effect is explicitly calculated, making the use of empirical parameters like μ^* obsolete. A metallic layer on a semiconducting substrate is conceptually different from a bulk in that, due to the lower dimensionality, there is a reduced phase space for low energy Coulomb scattering, that is repulsive for Cooper pairing (in s-wave), while the space for high energy scattering is not restricted, owing to the presence of the substrate. Therefore the Coulomb renormalization is unusually large in this type of system.

Discussion - The computed critical temperature for the undoped(doped) system as given in Tab. II is 3.42(3.54)K.

We have then shown that, releasing several unjustified approximations, the estimated critical temperature of 3.54K (doped system) is far too high as compared to the values experimentally observed 1.86K[4], 1.5K[6] and 1.1K[5].

What is the source of this mismatch? To answer this question we have to carefully investigate the effects not considered in the above analysis and their possible influence on superconductivity. I) We have assumed the RPA represent the screened Coulomb interaction. This is reliable in the high-density limit when screening is good. Therefore the Pb layer is expected to be well described. The approximation may be less accurate for the silicon hole band, since these states have a low density and, thus, will be poorly screened. However, the strong Coulomb repulsion will prevent a significant contribution to superconductivity, therefore this inaccuracy cannot affect the estimated T_c significantly. Surely not for the doped system where these bands do not even cross the Fermi level. II) In general, when computing the electron phonon pairing, vertex corrections can be safely dropped, due to Migdal's theorem[34, 35]. The shape of the Si hole pocket band might invalidate this conclusion. However, this cannot have a significant influence on the calculation of superconductivity in this system since, as discussed above, this band effectively does not take part in the condensation. Migdal's theorem is also not applicable in the small q limit. This does not affect the estimation of the phononic pairing, due to the small fraction of the Brillouin zone in which the problem occurs. Nevertheless we have to keep in mind that the low q physics are not correctly described under this assumption. III) In our calculations we do not include spin-orbit coupling effects. These have been shown to be relevant both for bulk lead[36, 37] and lead multilayers[38]. However the effect systematically increases the coupling strength, therefore it can not explain our overestimation of T_c . And actually its inclusion would lead to an even higher critical temperature. IV) In our work we consider only a statically screened Coulomb interaction. The result of dynamic (plasmonic) effects could lead to important modifications of the dielectric screening in the case of low energy surface plasmons. However, as first pointed out by Takada, this effect is known to give a positive contribution to superconductivity (enhancement of coulomb renormalization by the plasmonic peak[23, 39, 40]). Therefore, if relevant, it would lead to a higher estimate of T_c . V) Another questionable approximation is the use of the LDA in the low dimensional limit. This issue has been investigated in detail by Pollack and Perdew[41] showing that LDA performs well as soon as the ratio between the layer thickness and the r_s coefficient of the gas is ≈ 2 . In our case this ratio can be estimated to be of the order of 5 and we expect the LDA to perform as reliably as usual. VI) Due to the poor metal-substrate coupling, the calculated single particle excitation spectrum of Si presents a fundamental gap that is about one half of the observed gap in bulk silicon. This may lead to an overestimation in the Coulomb renormalization, and then in an overestimation of T_c . We have therefore accounted for this effect in our calculations by including a scissor correction on

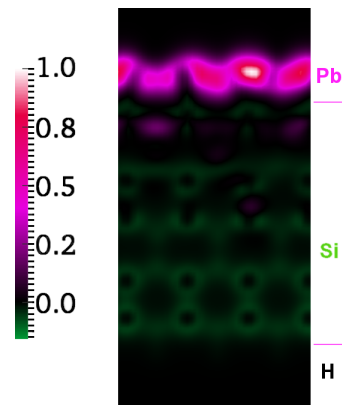


Figure 3. (color online) Real-space structure of the SC order parameter $\chi(\mathbf{R}, \mathbf{0})$ normalized to its maximal value of 0.0002765. As it can be interpreted as the wave function of condensed pairs the confinement of the SC phase to the Pb layer is clearly visible. The dark blue in the substrate indicates that it takes part in the Coulomb renormalization and thus reflects a proximity effect that extends throughout the whole substance.

the Si bands and the resulting effect on T_c correction is $< 0.1\text{K}$.

We believe that we have considered all relevant electronic pairing effects. In the bulk limit the critical temperature in SCDFT, using the same approximations as for the slab is 6.3 K that compares well with the experimental value of 7.2 K.

The only mechanism that is not included in our simulations and that, according to model calculations, is strongly suspected to suppress superconductivity, is the onset of fluctuations in the order parameter. While this could be in principle captured in SCDFT, the presence of infrared collective excitations of the order parameter is not accounted for in the present functionals. Owing to Mermin-Wagner's theorem[1, 42] these fluctuations completely forbid superconductivity in a strictly two dimensional system. In 3D systems of constrained geometry (such as surfaces) model calculations show that these fluctuations may still be relevant in the limit in which the thickness is of the atomic scale and the in-plane dimension of the system is macroscopic[43]. Due to the strong confinement of the SC phase to the lead layer, as is clearly seen in the real space structure of the order parameter of Fig. 1, one would expect to be in a regime where these fluctuation effects of the superconducting order parameter are relevant. While, as mentioned, neglecting vertex corrections has probably little effect on the phononic el-el coupling, effective interactions in the superconducting Nambu channel in the sense of the fluctuation propagator [44] can be very important. The disagreement between the calculated and experimental critical temperature then strongly suggests that T_c is experimentally limited by the fluctuation regime. The superconducting phase rapidly stabilizes with an increasing number of Pb

layers[45–47] strengthening this conclusion.

To summarize, we report a first-principles calculation of the superconducting ground state of a single lead layer deposited on a Si (111) substrate. We account for phonon mediated (via linear response DFT) and screened coulomb pairing (RPA) within the parameter free framework of Superconducting Density Functional Theory. We have shown that the isotropic approximation is not valid in this surface configuration, and in particular that the isotropic μ^* approximation used for bulk superconductivity leads to a large underestimation of the critical temperature. Our calculations predict a critical temperature about 80% larger than observed in experiment. Our analysis strongly suggests that this mismatch is attributed to the onset of long wavelength phase fluctuations of the superconducting order parameter.

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